# Effect of Temperature on the Performance of Limestone/Sandstone Filters Treating Landfill Leachate

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**Abstract:** The ability of limestone and limestone/sandstone filters to remove dissolved iron and manganese from landfill leachate under field conditions were investigated. The results showed that the precipitation of iron and manganese were affected by temperature and time. Most of iron was removed from solution within the first 10 min at 20°C while the removal of iron from solution took much longer time (50 min) at 5°C. Larger percentage (69%) of manganese was removed from solution within the first 20 min at 20°C compared to that (42%) removed at 5°C. Removal of manganese from solution was affected by the presence of iron while presence of manganese did not affect iron removal from solution. The lower removal efficiencies of manganese showed the slow kinetic of manganese oxidation. The iron and manganese removal rate constants of the limestone filters were higher than those of the limestone/sandstone filters. The pH of the water samples did not exceed 7.7. Therefore, the wetland ecosystem should be able to adjust to water having a slight alkalinity without suffering adverse effects.

Key words: Landfill leachate, iron, manganese, limestone, sandstone, filter

### INTRODUCTION

Landfill leachate is one of the main environmental concerns associated with landfill management because of its potential to damage the quality of both the ground and surface waters<sup>[1]</sup>. Contaminants in leachate include organic matter, heavy metals and mineral oils. However, the chemical composition of leachate varies greatly depending on the age of landfill and the events prior to the time of sampling which include the distribution of the organic components in landfill, the availability of nutrients, the moisture content of waste, moisture routing through the fill and the degree of initial compaction<sup>[2,3]</sup>.

Conventional water treatment systems that remove iron and manganese from wastewater involve the addition of alkaline chemicals (such as lime, sodium hydroxide and sodium carbonate) to the water. Alkali addition causes the pH of the water to increase and the dissolved metals to precipitate out of solution. These active systems usually have increased costs associated with their operation and maintenance, purchase of chemicals and disposal of metal laden sludge<sup>[4,5]</sup>. However, passive treatment systems that use limestone have become very popular for treating landfill leachates and mine drainage because these systems are inexpensive to construct and maintain and limestone is a cheap source of alkalinity<sup>[6,7]</sup>. Kamal<sup>[8]</sup> conducted a laboratory study to evaluate the effectiveness of

limestone filters in removing iron and manganese from landfill leachates under ambient temperature and found that most of these elements were removed from solution by precipitation within the first two hours. However, the effect of outdoor temperature variation on the precipitation of these metals must be investigated before a field scale filter is designed and constructed. The average water temperatures in Atlantic Canada fluctuate between 5 and 20 degrees during the months of March and November.

The aim of this study was to evaluate the effectiveness of limestone and limestone/sandstone filters in removing dissolved iron and manganese from a landfill leachate under field conditions. The specific objectives were: (a) to evaluate the impact of temperature variation (5-20°C) on the removal efficiencies of iron and manganese by limestone and limestone/sandstone filters, (b) to calculate the specific removal rates for Fe and Mn and (c) to determine the suitability of the treated wastewater for wetland aquatic life as measured by its final pH.

#### MATERIALS AND METHODS

## **Experimental apparatus**

The experimental setup shown in Fig. 1 consisted of six holding beakers each had a 12.5 cm diameter and a 15 cm height. Three beakers received limestone while the other three beakers received a mixture of limestone and

sandstone of 1:1 ratio. An aeration unit was installed at the bottom of each beaker. The air was provided from the main laboratory air supply to a manifold with six outlets. Each outlet was connected to a pressure regulator (Model 129121/510, ARO, Bryan, Ohio), which was connected to the aerator located in each holding beaker. Tygon tubing of 0.75 cm outside diameter was used to connect the main air supply, manifold and aeration unit.

## Preparation of leachate

The two heavy metals investigated in this study were iron and manganese. Contaminated water solutions were prepared using ferrous ammonium sulfate hexahydrate (Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O) and manganese sulfate monohydrate (MnSO<sub>4</sub>•H<sub>2</sub>O). They were purchased as reagent grade chemicals from Fisher Scientific, Ottawa, Ontario. Each chemical was dissolved in tap water which produced solutions with an iron concentration of 6.6 mg L<sup>-1</sup>, a manganese concentration of 1.8 mg L<sup>-1</sup> and an iron/manganese solution of 6.6/1.8 mg L<sup>-1</sup> as shown in Table 1.

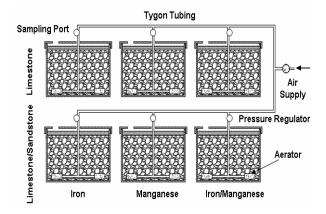


Fig. 1: Experimental setup

Table 1: Concentrations of elements present in the synthetic landfill leachate

Element	Synthetic Landfill Leachate (mg L <sup>-1</sup> )
Tap Water	
Aluminum	0.069
Arsenic	< 0.002
Chloride	7.000
Copper (Total)	0.010
Fluoride	0.060
Lead (μg L <sup>-1</sup> )	< 0.500
Mercury	< 0.050
Nitrate-Nitrogen	0.060
Sodium	8.000
Sulfate	11.800
Zinc (Total)	0.072
Regent Added	
Īron	6.60
or	
Manganese	1.80
or	
Iron (and)	6.60
Manganese	1.80

# **Experimental procedures**

Three beakers were filled with limestone (2.024 kg) while the other three beakers were filled with a mixture of limestone (1.012 kg) and sandstone (1.012 kg), each to a height of 15 cm. A 0.9 L iron solution (6.6 mg L<sup>-1</sup>) was poured into each of the first set of two beakers, a 0.9 L manganese solution (1.8 mg L<sup>-1</sup>) was poured into each of the second set of two beakers and a 0.9 L iron/manganese solution (6.6 and 1.8 mg L<sup>-1</sup>) was poured into each of the third set of two beakers. The pressure regulator on the aeration system was adjusted to provide an aeration rate of 7 cm<sup>3</sup> min<sup>-1</sup>. The experiment was conducted for 3 hrs under four different temperatures (5, 10, 15 and 20°C). A total of 24 beakers were used in this study. The experiment was replicated three times.

Water samples of 5 mL were collected from each beaker at 2.5, 5, 7.5, 10, 20, 30, 40, 50, 60, 80, 100, 120, 150, 180 min and were immediately stored in the freezer to slow the iron oxidation reactions. The samples were analyzed for iron and manganese using a spectrophotometer (Model DR/2500, HACH Company, Loveland, CO, USA). The FerroVer® Method (Method 8008) was used to measure total iron and the Periodate Oxidation Method (Method 8034) was used to measure manganese. The pH of the samples was also measured using a pH meter (Model 805MP, Fisher Scientific, Montreal, Quebec, Canada).

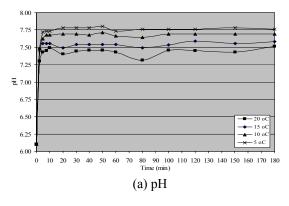
# RESULTS AND DISCUSSION

Figure 2 -7 present the changes in the pH and the iron and manganese concentrations in the wastewater over time. Table 2 and 3 show the removal efficiencies of iron and manganese.

## Iron

The iron concentrations in the water samples obtained from the limestone filters after 3 hrs were 0.02, 0.07, 0.23 and 0.23 mg L<sup>-1</sup> with average removal efficiencies of 99.77, 98.94, 96.52 and 96.52% for the temperatures of 20, 15, 10 and 5°C, respectively. The iron concentrations in the water samples obtained from the limestone/sandstone filters after 3 hrs were 0.05, 0.07, 0.23 and 0.34 mg L<sup>-1</sup> with average removal efficiencies of 99.32, 98.94, 96.52 and 94.85% for the temperatures of 20, 15, 10 and 5°C, respectively. Removal of iron from the solution containing iron and manganese was similar to that of the solution containing iron alone for both the limestone and the limestone/sandstone filters.

The iron removal efficiency decreased as the temperature decreased. Most of iron was removed from solution within the first 10 min at 20°C while the removal of iron from solution at 5°C took much longer time. However, by the end of the experiment (180 min) the difference in iron removal due to the effect of temperature (20°C vs. 5°C) was approximately 4.92%.



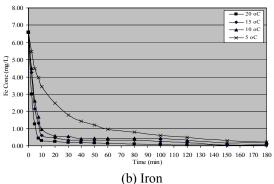
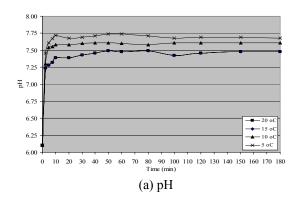


Fig. 2: pH and iron concentrations of water obtained from the limestone filter treating manganese free wastewater



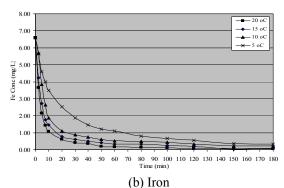
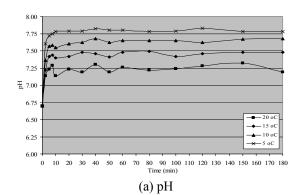


Fig. 3: pH and iron concentrations of water obtained from the limestone/sandstone filter treating manganese free wastewater



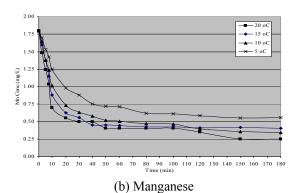
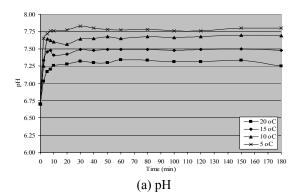


Fig. 4: pH and manganese concentrations of water obtained from the limestone filter treating iron free wastewater



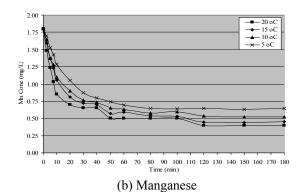


Fig. 5: pH and manganese concentrations of water obtained from the limestone/sandstone filter treating iron free wastewater

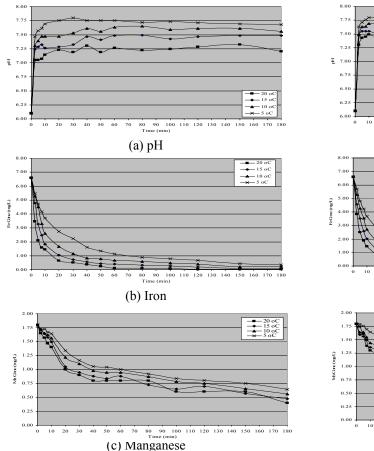


Fig. 6: pH and iron and manganese concentrations of water obtained from the limestone/sandstone filter treating Fe and Mn containing wastewater

These results are very useful when designing the field filters because the runoff during the winter is slower and the temperature of the water is lower, compared to those during the summer, thus requiring a longer retention time for iron removal.

Iron usually drains from landfills in the reduced ferrous form (Fe<sup>2+</sup>). At a pH greater than 3.5 with oxygen present, ferrous iron will oxidize to ferric iron as follows<sup>[5]</sup>:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(1)}$$
 (1)

Ferric iron forms iron hydroxide (Fe(OH)<sub>3</sub>) precipitate as a result of hydroxylation (Fe<sup>3+</sup> reacting with  $H_2O$  molecules) as follows<sup>[9]</sup>:

$$Fe^{3+}_{(aq)} + 3 H_2O_{(1)} \rightarrow Fe(OH)_{3(s)} + 3H^{+}_{(aq)} (Acidity)$$
 (2)

Cravotta and Trahan<sup>[6]</sup> indicated that the oxidation of iron in surface waters can be described by the following differential rate expression:

$$dC/dt = K C (3)$$

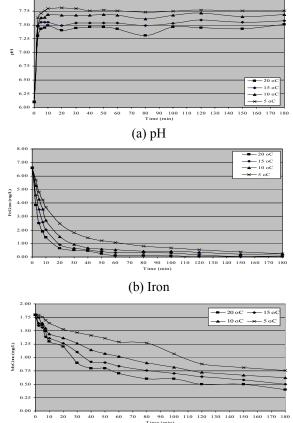


Fig. 7: pH and iron and manganese concentrations of water obtained from the limestone/sandstone filter treating Fe and Mn containing wastewater

(c) Manganese

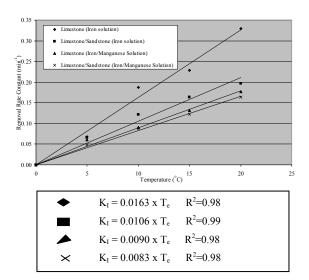


Fig. 8: Effect of temperature on iron removal rate constants

#### Where

C = Element concentration in the solution (mg  $L^{-1}$ )

= Oxidation rate constant (min<sup>-1</sup>)

Table 2: Iron removal efficiency (%)

		Mn free wastewater							Mn containing wastewater							
Time	20 °C		15 °C		10 °C		5	5 °C		20 °C		15 °C		10 °C		°C
	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF
2.5	54.55	44.55	35.30	36.06	31.67	13.94	16.97	14.70	47.58	41.67	27.58	30.91	20.00	20.00	16.97	13.64
5	80.76	67.42	67.58	58.79	60.30	41.82	31.97	30.45	68.33	61.97	50.45	46.67	31.67	35.45	28.33	27.27
7.5	93.48	78.48	80.00	73.48	74.55	60.15	40.00	39.39	75.91	71.36	62.73	60.76	50.15	46.36	37.12	36.06
10	95.45	83.71	90.91	77.88	85.45	71.82	47.73	46.97	77.88	77.88	72.27	69.39	60.61	58.79	43.79	44.39
20	96.29	90.68	92.88	88.48	91.21	83.33	62.42	61.67	90.15	90.15	84.09	86.21	74.85	77.27	58.64	62.42
30	96.97	93.71	95.00	90.91	91.82	86.67	72.73	71.82	92.12	92.12	88.94	90.15	82.58	85.91	66.36	72.73
40	97.12	94.70	94.85	92.58	93.94	88.94	78.48	77.73	94.39	93.03	91.52	91.82	87.42	89.85	75.76	78.48
50	97.58	97.05	95.00	93.94	93.18	90.91	81.82	81.52	96.21	96.21	93.33	93.94	88.18	91.06	79.70	81.82
60	97.88	97.65	95.00	95.00	93.48	92.12	85.45	83.33	98.18	98.18	93.94	95.00	90.00	91.97	83.03	83.79
80	98.18	97.95	95.00	95.00	93.48	92.58	87.88	87.88	98.33	98.33	95.00	95.00	90.91	93.48	86.67	87.88
100	98.64	98.18	96.06	96.06	93.48	93.48	90.91	90.00	98.79	98.79	96.06	95.45	92.58	93.48	88.18	89.85
120	99.02	98.56	96.97	96.97	95.00	94.85	92.42	91.82	99.39	99.39	96.97	97.73	93.94	94.70	90.00	91.82
150	99.32	98.86	99.55	99.55	97.42	96.67	95.45	94.39	99.39	99.39	98.94	99.55	96.67	96.67	93.33	94.39
180	99.77	99.32	98.94	98.94	96.52	96.52	96.52	94.85	99.70	99.70	98.94	99.00	96.52	96.40	94.85	96.01

LF = Limestone filter

LSF = Limestone/sandstone filter

Table 3: Manganese removal efficiency (%)

	Fe free wastewater								Fe containing wastewater							
Time	20	°C	15	°C	10	°C	5	°C	20	°C	15	°C	10	)°C	5	°C
•	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF	LF	LSF
2.5	17.44	17.44	11.39	11.39	8.67	8.67	5.67	5.67	8.56	3.22	4.22	11.39	5.17	8.67	5.67	0.67
5	31.11	31.11	23.44	23.44	23.44	23.44	15.06	15.06	12.78	10.83	8.67	13.33	8.39	8.61	4.44	2.22
7.5	42.61	42.61	36.22	31.78	31.50	28.89	21.11	21.11	18.44	17.22	12.44	22.94	9.94	14.06	7.11	5.78
10	61.11	52.78	51.11	41.28	43.61	38.83	30.50	28.61	22.22	27.78	17.00	24.44	13.17	20.00	8.89	8.61
20	69.44	61.11	65.44	55.00	59.39	50.06	45.61	41.61	44.44	33.33	42.00	29.67	32.33	24.22	25.61	15.33
30	72.22	63.89	69.11	60.00	64.78	57.78	51.33	51.33	50.00	50.00	47.28	38.89	38.72	29.67	35.56	18.50
40	72.22	63.89	74.83	60.94	67.78	59.22	58.39	55.56	55.56	55.56	51.11	49.06	45.39	36.67	41.28	21.67
50	77.78	72.22	74.83	68.33	71.44	63.78	60.00	58.83	55.56	55.56	53.61	49.72	47.33	40.44	42.22	24.44
60	77.78	72.22	75.56	67.28	72.11	64.83	60.61	61.33	55.56	61.11	51.11	53.33	47.61	43.33	44.44	28.39
80	77.78	72.22	76.50	70.11	73.83	68.00	65.56	64.11	55.56	66.67	60.00	57.78	51.44	50.00	48.89	29.33
100	77.78	72.22	76.50	70.44	74.17	66.94	66.22	64.44	66.67	66.67	63.78	60.83	56.56	54.50	53.33	40.78
120	80.56	77.78	77.17	75.06	78.17	70.11	67.67	64.11	66.67	72.22	61.33	64.44	58.50	60.00	55.28	51.11
150	86.11	77.78	76.83	75.56	80.22	70.83	69.39	64.83	66.67	72.22	68.33	67.83	63.61	62.78	58.50	55.11
180	86.11	77.78	77.78	74.67	80.89	70.83	68.89	64.11	77.78	77.78	73.61	72.28	68.89	65.61	64.44	58.00

LF = Limestone filter

LSF = Limestone/sandstone filter

Equation (3) on integration yield the following exponential equation:

$$C_{\text{Fet}} = C_{\text{Fei}} e^{-\text{KI t}} \tag{4}$$

Where:

 $C_{\text{Fet}} = \text{Iron concentration at time t (mg L}^{-1})$ 

 $C_{\text{Fei}} = \text{Iron initial concentration (mg L}^{-1})$ 

The experimental data was fitted to Equation (4) and the iron removal rate constants were calculated (Fig. 8).

Increasing the temperature increased the iron removal rate constant while the presence of manganese in the solution decreased the iron removal rate constant due to the competition between iron and manganese ions. The results also showed higher iron removal rate constants in the limestone filter compared to those of limestone/sandstone.

Analysis of variance (ANOVA) was performed on the iron removal rate constant data using MINITAB Release 14 (MINITAB Inc., State College, PA).

Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 4) showed that the

filter type, solution type and temperature have significant effects on the removal rate constants (P = 0.04, 0.005, 0.0001, respectively). The results showed no significant interactions between the factors. The results of Duncan's Multiple Range test (Table 5) showed that the means of the filter types, solution types and temperatures were significantly different from one another at a 95 % confidence level.

Table 4: Analysis of variance of the iron removal rate constant data

Source	DF	SS	MS	F- Value	P
Total	15	0.08267	0.00551		
Filter Type (F)	1	0.00580	0.00580	5.32	0.0440
Solution Type (S)	1	0.01429	0.01429	13.11	0.0050
Temperature (Te)	3	0.05165	0.01721	15.78	0.0001
F x S	1	0.00323	0.00323	0.65	0.4350
F x Te	3	0.00216	0.00072	0.25	0.8590
S x Te	3	0.00339	0.00113	0.68	0.5880
Error	10	0.01091	0.00109		

DF = Degrees of Freedom

SS = Sum of Squares

MS = Mean of Squares

 $R^2 = 0.87$ 

CV = 2.55 %

Table 5: Differences among the means of the filter types, solution types and temperatures

types and temperatures			
Parameter	Number of Observations	Iron Removal Rate Constant	Duncan Grouping
Filter Type			
Limestone	8	-0.159225	A
Limestone/Sandstone	8	-0.121132	В
Solution Type			
Iron	8	-0.170075	A
Iron/Manganese	8	-0.110288	В
Temperature (°C)			
5	4	-0.060875	Α
10	4	-0.121800	В
15	4	-0.161500	C
20	4	-0.216550	D

Means with the same letter are not significantly different from each other at 95% confidence level

Although several researchers<sup>[10,11]</sup> suggested that the use of a mixture of limestone and sandstone to treat iron contaminated wastewater in order to avoid armoring of limestone and to increase the lifetime of the filter, the result obtained from this study showed that increasing the percent of limestone in the filter from50% to 100% increase the iron removal rate constant by 38%. The precipitation reaction of ferric hydroxide (Fe(OH)<sub>3</sub>) produced protons that would consequently decrease the pH of the solution and increase the solubility of Fe(OH)<sub>3</sub>. However, in the presence of limestone stone, the protons produced from precipitation reaction were consumed by the calcium carbonate dissolution reaction as shown in the following equation:

$$CaCO_3 + 2 H^+ \rightarrow Ca^{2+} + H_2CO_3$$
 (5)

As the limestone increased, the neutralization capacity of the solution increased (the pH of the solution increased). The results showed that the higher the pH of the solution the lower the solubility of Fe(OH)<sub>3</sub> and therefore, the higher the removal rate constant.

Sasowsky *et al.*<sup>[11]</sup> reported that sandstone has more negative surface charge than limestone. This would indicate that in addition to more rapid aqueous Fe<sup>2+</sup> oxidation at pH > 6.5 due to increased hydroxide ion, the decrease in zeta potential (i.e. surface charge) with increasing pH would promote Fe<sup>2+</sup> surface reaction. A synergistic effect clearly occurs when limestone and sandstone are mixed, promoting the precipitation of metal oxide on the sandstone, while allowing the limestone to remain uncoated and continue neutralizing the solution.

#### Manganese

The manganese concentrations in the water samples obtained after 3 hrs from the limestone filters were 0.25, 0.40, 0.34 and 0.56 mg L<sup>-1</sup> with average removal efficiencies of 86.11, 77.78, 80.89 and 68.89% for the temperatures of 20, 15, 10 and 5°C, respectively. The manganese concentrations in the water samples obtained after 3 hrs from the limestone/sandstone filters were 0.40, 0.46, 0.53 and 0.65 mg L<sup>-1</sup> with average total removal efficiencies of 77.78, 74.67, 70.83 and 64.11% for the temperatures of 20, 15, 10 and 5°C, respectively. Most of the manganese (41.61-69.44%) was removed from solution by the filters within 20. However, removal of manganese from the solutions containing iron and manganese was lower than that from solutions containing manganese alone.

The manganese removal efficiency decreased as the temperature decreased. However, by the end of the experiment (180 min). The results should lower manganese removal in the presence of iron. This is because Fe<sup>2+</sup> controlled Mn oxidation rates by contributing electrons to previously precipitated Mn oxides to produce Mn<sup>2+</sup> as reported by Burdige *et al.*<sup>[12]</sup>. Barton and Karathanasis<sup>[13]</sup> also reported Mn oxidation inhibition during the presence of Fe<sup>2+</sup> within the system. The relatively lower removal efficiencies of manganese observed in this experiment compared to iron show the slow kinetics of Mn<sup>2+</sup> oxidation as reported by Stumm and Morgan<sup>[14]</sup>.

According to Stumm and Morgan<sup>[14]</sup>, the oxidation of manganese in surface waters can also be described by Equation 4. The manganese data were, therefore, fitted into Equation (4) and the manganese removal rate constants were calculated (Fig. 9). Increasing the temperature increased the manganese removal rate constant while the presence of iron in the solution decreased the manganese removal rate constant.

Analysis of variance (ANOVA) was performed on the manganese removal rate constant data using MINITAB Release 14 (MINITAB Inc., State College, PA). Duncan Multiple range test was also performed on the data to test the differences among the levels of each factor. The ANOVA results (Table 6) showed that the filter type, solution type and temperature had significant effects on the removal efficiency (P = 0.05, 0.0001 and 0.001, respectively). There were no interactions between the factors. The results of Duncan's Multiple Range test (Table 7) showed that the means of the filter types, solution types and temperatures were significantly different from one another at a 95% confidence level.

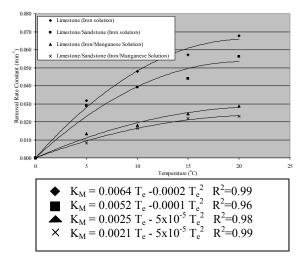


Fig. 9: Temperature effect on manganese removal rate constants

Table 6: Analysis of variance of the manganese removal rate constants

Source	DF	SS	MS	F- Value	P
Total	15	0.004572	0.000305		
Filter Type (F)	1	0.000158	0.000158	7.61	0.0200
Solution Type (S)	1	0.003011	0.003011	144.86	0.0001
Temperature (Te)	3	0.001194	0.000398	19.15	0.0001
F x S	1	0.000026	0.000026	0.23	0.6410
F x Te	3	0.000012	0.000003	0.01	0.9990
S x Te	3	0.000148	0.000049	1.82	0.2220
Error	10	0.000207	0.000021		

DF = Degrees of Freedom

SS = Sum of Squares

MS = Mean of Squares

 $R^2 = 0.95$ CV = 1.39 %

As in the case of iron, the limestone filters had higher removal rate constants than those of limestone/sandstone filters. Increasing the percent of limestone increased the pH and thus, reduced the solubility of MnOOH which resulted in a higher removal rate constant. According to Gazea *et al.*<sup>[5]</sup>, one possible mechanism for abiotic manganese precipitation involves the oxidation of Mn<sup>2+</sup> to either Mn<sup>3+</sup> or Mn<sup>4+</sup>, which is similar to ferrous iron oxidation. Then, the

Table 7: Differences among the filter types, solution types and temperatures

Parameter	Number of Observations	Mn Removal Rate Constant	Duncan Grouping
Filter Type			
Limestone	8	0.0362	A
Limestone/Sandstone	8	0.0299	В
Solution Type			
Iron	8	0.0467	A
Iron/Manganese	8	0.0193	В
Temperature (°C)			
5	4	0.0206	A
10	4	0.0305	В
15	4	0.0369	C
20	4	0.0441	D

Means with the same letter are not significantly different from each other at 95% confidence level

trivalent (Mn<sup>3+</sup>) or tetravalent (Mn<sup>4+</sup>) form precipitates as MnOOH.

In alkaline environments, Mn<sup>2+</sup> can also precipitate in the carbonate form, which in the presence of oxygen may also further oxidize to MnO<sub>2</sub> as follows:

$$Mn^{2+} + HCO_3 \rightarrow MnCO_{3(s)} + H^+$$
 (6)

$$MnCO_3 + O_2 \rightarrow MnO_2 + CO_2 \tag{7}$$

# pН

The initial pH of the iron, manganese and iron/manganese solutions were 6.1, 6.7 and 6.1 which increased to 7.3-7.8, 7.2-7.8 and 7.20-7.76 during the experiment, respectively. The final pH values were 7.68-7.76, 7.61-7.69, 7.48-7.58 and 7.26-7.51 for the iron solution, 7.78-7.80, 7.68-7.69, 7.48-7.50 and 7.19-7.29 for manganese solution and 7.68-7.76, 7.56-7.69, 7.48-7.58 and 7.21-7.51 for the iron/manganese solution at the temperatures of 5, 10, 15 and 20°C, respectively. As pH of the solution increased, the dissolved iron and manganese concentration decreased. The results showed good correlations ( $R^2 = 0.86-0.93$ ) between the removal efficiencies of iron and the pH of the solutions in all filters. No consistent correlations were observed between the removal efficiencies of manganese and the pH of the solution. Correlation between iron removal efficiency and pH was reported by several authors<sup>[6,15]</sup>. Aziz and Smith<sup>[16]</sup> and Cravotta and Trahan<sup>[6]</sup> found no correlation between the manganese removal efficiency and the pH of the solution.

During the experiment, the pH of the water samples did not exceed 7.7. Presently, the pH of the water in the wetland is approximately neutral. According to Kadlec and Knight<sup>[17]</sup>, many treatment bacteria are not able to survive in highly acidic environments (pH < 4.0) or highly alkaline environments (pH > 9.5). Tanner<sup>[18]</sup> suggests that the optimum pH range for treatment wetlands is 3.0 < pH < 10.0. Therefore, the wetland ecosystem should be able to adjust to the treated water which has a slightly higher pH (7.7) without suffering any adverse effects.

#### **CONCLUSION**

The limestone and limestone/sandstone filters were effective in removing dissolved iron and manganese from landfill leachate under field conditions. The results obtained from these experiments showed that the time and temperature have significant effects on the iron and manganese removal efficiencies. Most of iron was removed from solution within the first 10 min at 20°C while the removal of iron from solution took much longer time (50 min) at 5°C. Larger percentage (69%) of manganese was removed from solution within the first 20 min at 20°C compared to that (42%) removed at 5°C. Removal of manganese from solution was affected by the presence of iron while presence of manganese did not affect iron removal from solution. The lower removal efficiencies of manganese showed the slow kinetic of manganese oxidation. The iron and manganese removal rate constants of the limestone higher filters were than those of limestone/sandstone. The pH of the water samples did not exceed 7.7. Therefore, the wetland ecosystem should be able to adjust to water having a slight alkalinity without suffering adverse effects.

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